The January 2, 1992, Explosion in a Deuterium / Palladium Electrolytic System at SRI International

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ABSTRACT

This paper reviews the accident that occurred at SRI International on January 2, 1992. A plausible explanation for the cause of the accident is proposed, and recommendations are made pertaining to the safety of future experiments. These recommendations relate to the design of electrolysis experiments, and to the behavior of recombination catalysts, and may provide useful guidelines for other workers in the field.

INTRODUCTION

On January 2, 1992, an electrochemical cell exploded during an experiment at SRI International in Menlo Park, California.[1] There was no major structural damage, fire, or release of toxic or radioactive materials, but one scientist, Dr. Andrew Riley, was killed when he was hit by a six-inch-long steel cylinder (a part of the cell container) which was propelled upward after the cell burst. Three other scientists were slightly injured by flying glass and other debris.

A diagram of the cell, which was placed inside a flow calorimeter, is shown in Figure 1. On January 1, it was noticed that gas was leaking from the tube which joined the cell to the pressure transducer; the tube was cut and a Swagelok union and endcap was fitted loosely using PTFE ferrules to the remainder of the gas tube.

FRONTIERS OF COLD FUSION

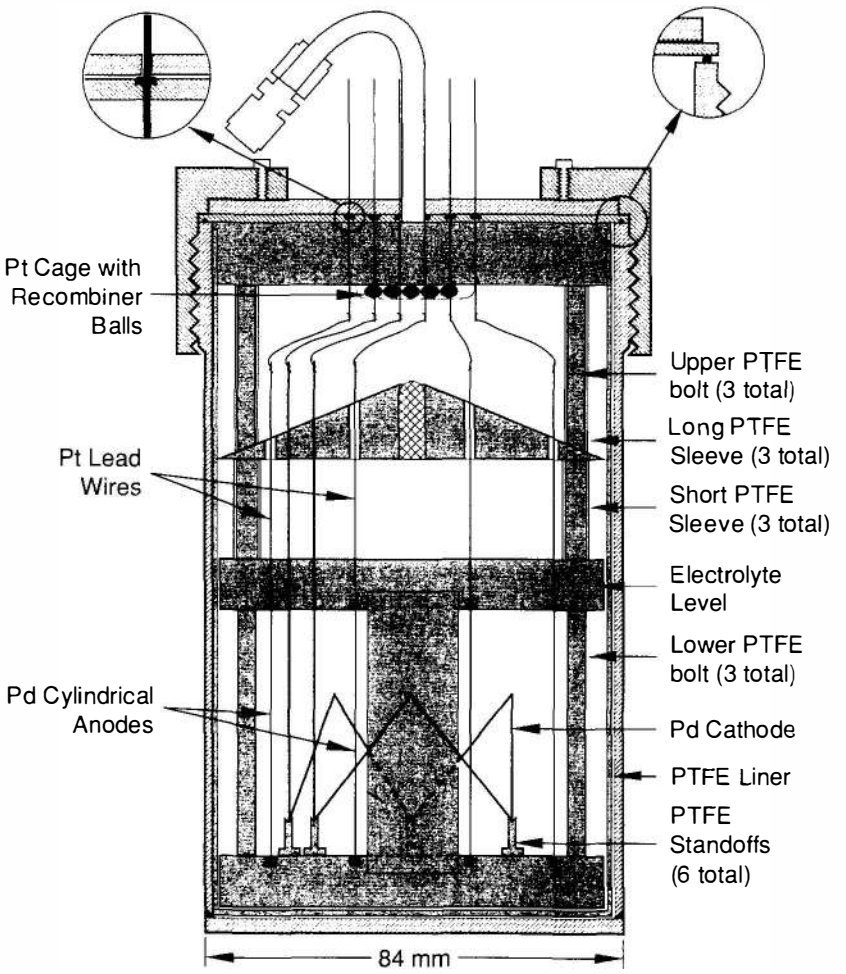

Figure 1. Cell before explosion (actual size).

The assembly was returned to the bath, subsequent to more complete repair the next day.

On January 2, another leak was observed. Dr. Riley first removed the clear acrylic top of the calorimeter and then lifted the calorimeter out of the water bath, set it on the edge of the bath, and was waiting for the water to drain back into the bath when the explosion occurred.

THE INVESTIGATION

Immediately after the accident, checks were made to determine whether nuclear products were associated with the event. Tests were performed on the dosimeters worn by the experimenters, wipes taken from the accident area, fluids from the area, and various internal components of the cell, for evidence of radiation. All showed radiation levels at background values. From these determinations, it was concluded that there was no measurable release of radiation at the time of the accident.

Metallurgical And Mechanical Examination

In order to assess the energy and pressure changes associated with the explosion, the deformation of the cell recovered from the accident was measured and modeled with SRI's proprietary computational codes.[2] The circumference of the cell was measured at several axial locations as shown in Figure 2. The maximum circumferential strain was 12.5% and was located in the top half of the cell, which, during use, contained mostly gas.

SRI's "L2D" code was used to model the effects of the explosion. This code was specially designed to calculate the effects of explosions on materials and structures. The stainless steel was modeled as an elastic-plastic material with work hardening, the PTFE components were generally modeled with zero strength, and the water and gas were modeled by appropriate equations of state.

Two types of scenarios were calculated with the L2D code. In the first type, thermal energy was taken to be deposited in the electrolyte over a short time, creating a high pressure steam bubble in the liquid. The results showed that the largest shell deformation was produced in the lower half of the cell, i.e., in that part of the cell containing the liquid. This

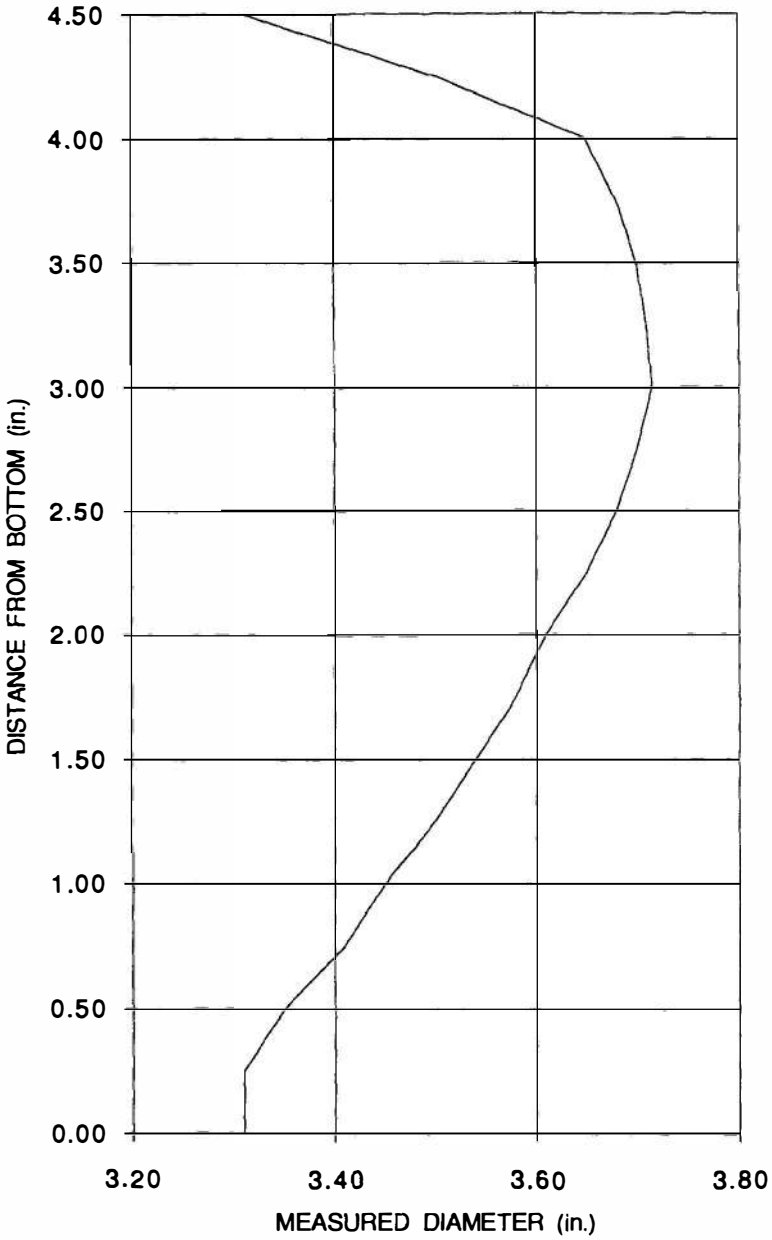

Figure 2. Measured deformation of cell diameter.

disagreement between the calculated location of the region of peak deformation and the actual observation on the cell, led us to conclude that a steam explosion did not substantially contribute to the accident.

In the second scenario, the case of a deuterium-oxygen explosion in the upper part of the cell was considered. In all calculations the initial pressure after detonation was taken to be 10 times the gas pressure before detonation or one half the Chapman-Jouget pressure. Comparison was made of the deformation calculated for a detonation initiated at the bottom (and at the top) of the gas volume and propagating at a velocity of 800 m/s, with that calculated for a constant volume (instantaneous) explosion. The calculated deformations for the two cases were identical. Therefore, all subsequent calculations were performed with constant volume explosions and with the equation of state of the polytropic gas.

A series of calculations were made for different initial gas pressures that produced different final deformations. The final deformation that most closely corresponds to the observed deformation is shown in Figure 3. The initial pressure in this calculation was approximately 300 atm, which corresponds to a pressure of approximately 30 atm before detonation. Comparison of Figures 2 and 3 shows that the calculated shape of the cell matches the observed shape reasonably well. In particular, the location and amplitude of the peak strain agree. For this case, the velocity imparted to the upper part of the cell which induced the fatality was calculated to be 25 m/s.

Table 1 shows the partitioning of the energy during the explosion. The format of this table is such that the shaded terms in each section are partitioned into the components shown in the next lower section of the table.

Conditions in the Cell at the Time of the Explosion

A comprehensive set of data was recorded for the cell over the entire 865 hr duration of the experiment (designated C1).[3] At 780 hr (event A in Figure 4), the pressure transducer recorded a rapid transient down to nominally 1 atm. The calorimeter net output power curve at 780 hr (event A in Figure 5) moved in the endothermic direction by about the correct power (0.16 W) for loss of the heat of recombination as a result of the loss of gas. This event is likely to be a transient leak of unknown origin.

Table 1. Energy partitioning (in J).

BEFORE EXPANSION	Total Internal Energy in gas		39700
PARTITIONING OF TOTAL INTERNAL ENERGY AFTER EXPANSION	PV work done on cell		3700
	Internal Energy of gas at time of venting		36000
PARTITIONING OF PV WORK DONE ON CELL	Strain Energy Absorbed		
	Shell	1620	
	Cover	110	
	Other	240	1970
	Energy to shear weld		100
	Kinetic Energy of cell		
	Top	760	
	Bottom	750	
	Cooling fins & water	140	
	Other	20	1670
			3740
PARTITIONING OF KINETIC ENERGY OF TOP OF CELL	Energy absorbed by head impact		300–700
	Energy to reach ceiling		50
	Energy to deform top of cell		10
	Energy to deform concrete		10
	Total		370–770

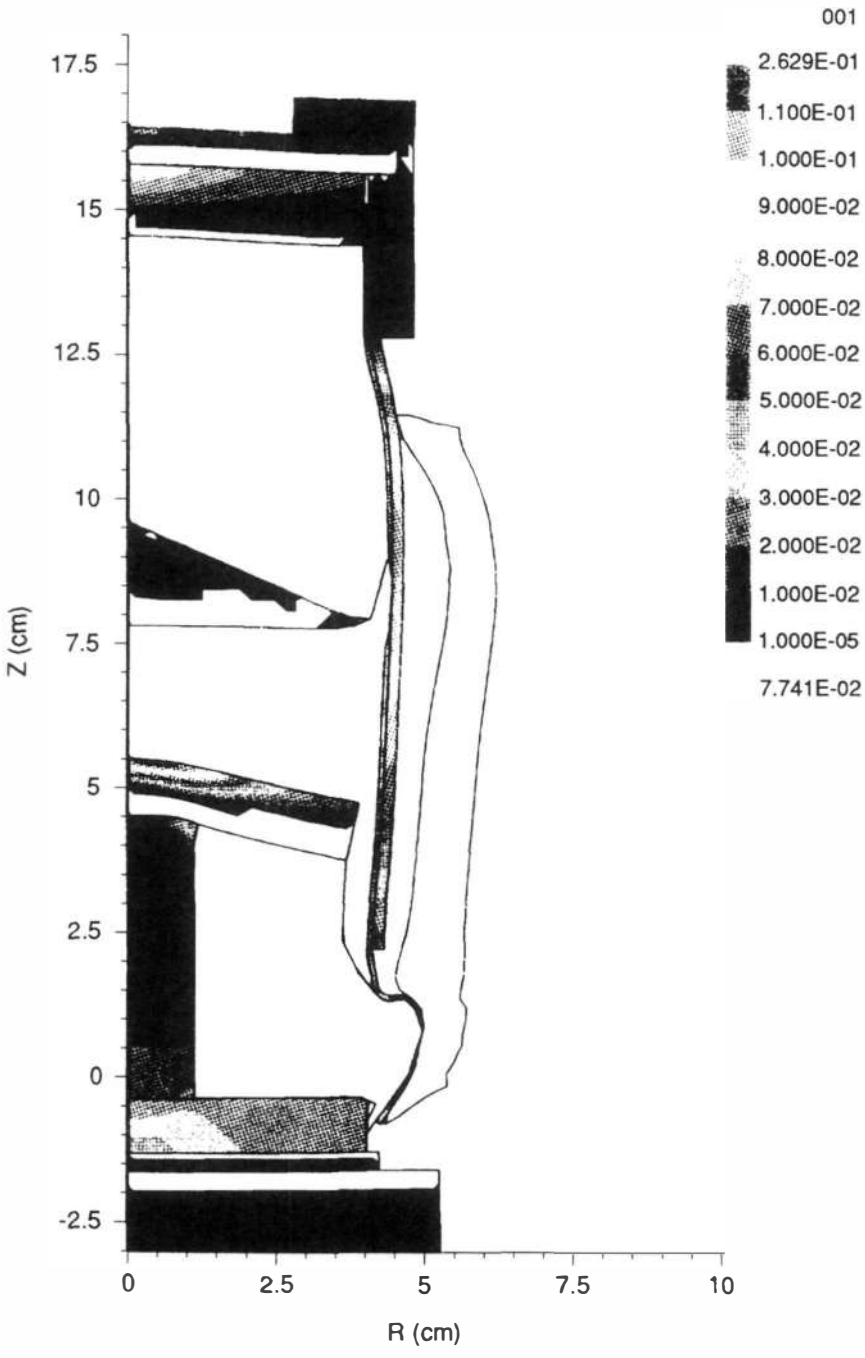

Figure 3. Computed deformed shape and contour plots of permanent strain from explosion of deuterium-oxygen at 30 bars.

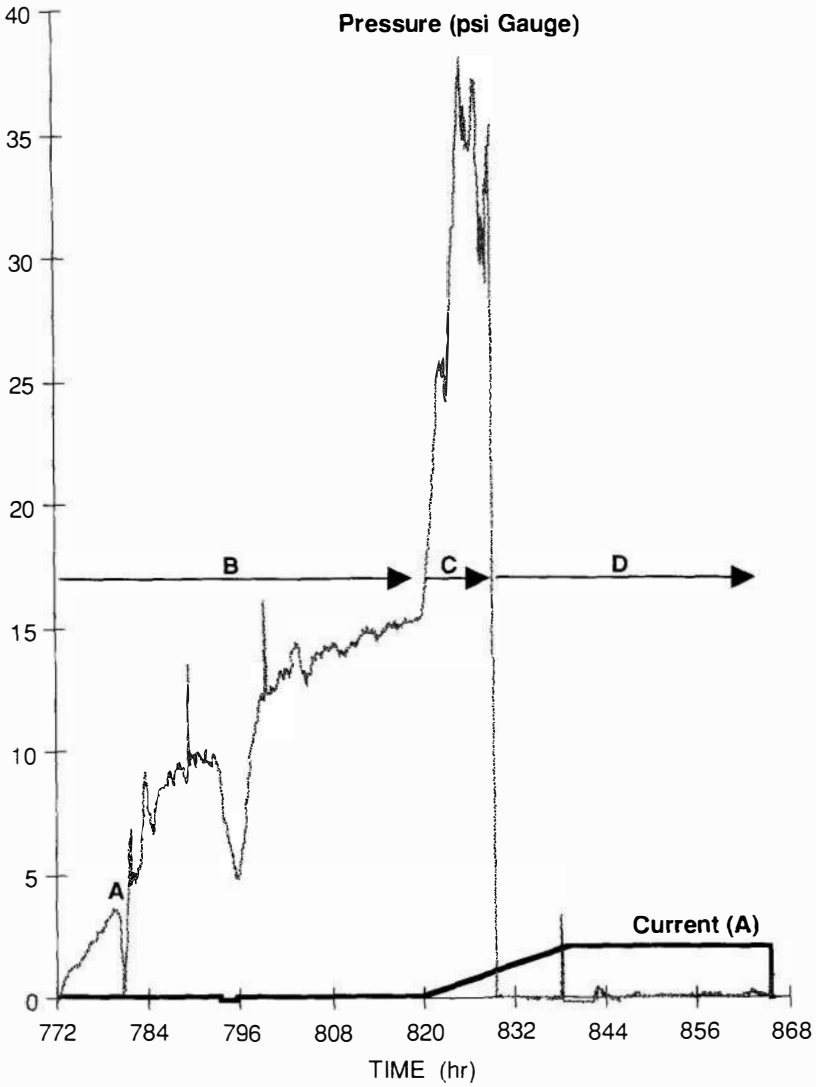

Figure 4. Current and gauge pressure at times following current step down.

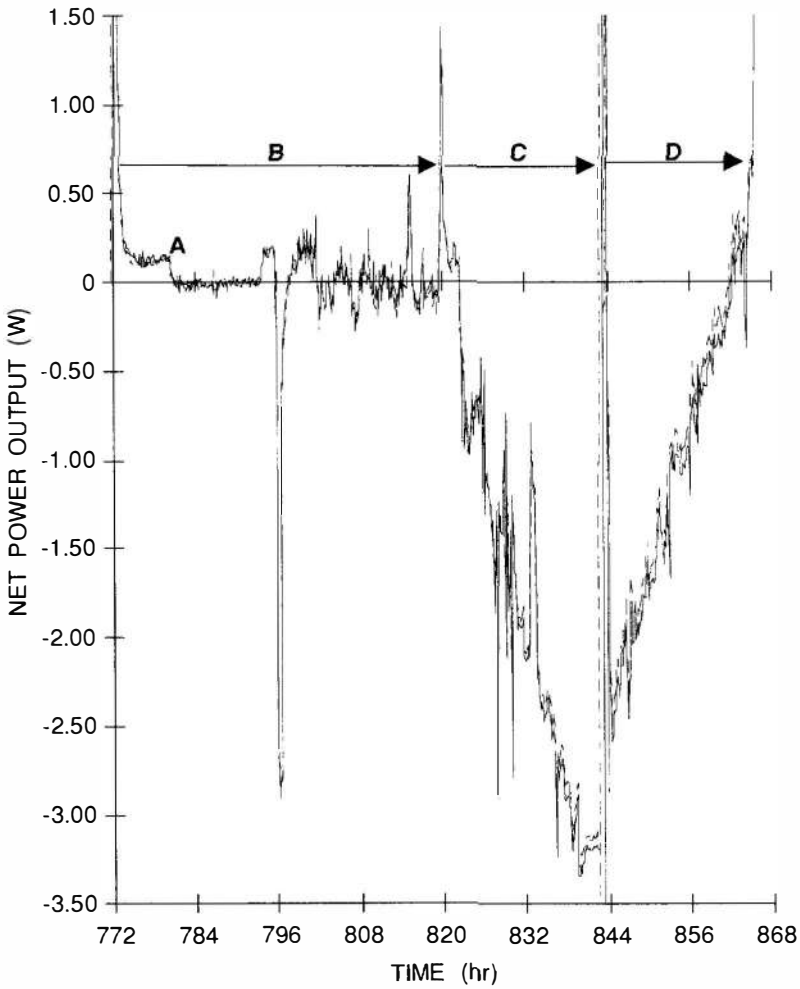

Figure 5. Excess power (W).

The pressure recovered at rates consistent with the electrolysis rate, but the power curve did not recover, suggesting that the catalyst cooled during the pressure transient and never recovered its initial activity. The pressure after 772 hr, until the obvious development of a major leak in the transducer/gas inlet tubing at 829 hr, increases, indicating that the activity of the recombination catalyst remained low. The net power record shows increasingly endothermic heating rates from 820 to 844 hr (event C in Figure 5), consistent with loss of recombination and the evolution of about 0.5 liters of stoichiometric gas.

The net power record following repair of the gas leak at 844 hr (event D in Figure 5), is hard to understand. The gradual, increasingly exothermic, progression of the net power suggests that, for this period, recombination was occurring in direct proportion to the pressure. Assuming that all leaks were effectively plugged, the rate of pressure increase inside the cell would have continued at about 4 atm/hr upon repair at 844 hr, decreasing to 0 atm/hr at 862 hr. This would indicate that the cell was pressurized with about 30 atm of stoichiometric gas (deuterium/oxygen) on the morning of January 2.

Several observations remain unexplained by the above scenario. The slow, almost linear, increase in recombination rate over the final 20 hr operation at a current of 2.1 A is not representative of normal recombination catalyst behavior. Under very high pressures of stoichiometric gas, increases in catalyst temperature caused by the highly exothermic reaction lead inevitably to rapidly accelerating rates. The observed behavior is more consistent with phenomena expected if the reaction quickly becomes limited by mass transport, e.g., if the active surface area was very small, such as a Pt wire surface, or if the active regions were in thermal contact with the cell wall, e.g., flakes or fragments contacting the wall or oxides on the wall surfaces. Alternatively, if the pressure reached 30 atm, the dissolution of gas in the electrolyte could lead to sufficient flux of oxygen to the cathode (and conversely deuterium to the anode) where recombination might occur.

CONCLUSIONS

The computed shape of the deformed cell for energy releases in the electrolyte with a range of pressures and locations, show that deformation would be concentrated in the bottom of the cell, unlike the deformation observed in the accident. In contrast, the

computed shape for a 30 atm mixture of deuterium-oxygen that detonates in the gaseous portion of the cell agrees approximately with the observed deformation.

Observations and calculations of the physical evidence from the explosion are largely consistent with the hypothesis that, over a period of time, a stoichiometric mixture of deuterium and oxygen built up in the cell, to a pressure of approximately 30 atm, and a detonation was initiated in the gas causing an approximately stepped pressure rise to about 300 atm. The detonation may have been initiated by physical effects associated with removing the cell from the water bath.

This hypothesis is not immediately consistent with the following observations:

Mass balance considerations show that a leak from the cell of about 0.1 cm^3/s would ensure no net pressure rise in the interval 843-865 hr; the cell was observed at 864 hr, and later, to have a leak that appeared to be sourced from a volume not significantly above 1 atm, at a rate that has been estimated to be between about 0.1 and 0.3 cm^3/s.

For the electrolysis of water, the pressure coefficient of cell voltage is not less than about 45 mV/decade of pressure. The cell voltage immediately preceding the accident was smaller than it had been at 844 hr at which time the cell had apparently been opened to ambient pressure. This indicates that, if anything, the pressure had gone down before the accident and not up. However, note that for a cell reaction which involves the simultaneous oxidation of D_2 and reduction of D_2O deuterium, the pressure coefficient of voltage is lower.

For several hours before the accident, recombination had been occurring, apparently at a rate of approximately 3.5 W, and presumably near the pressure of the explosion, thought to be 30 atm. It is not obvious how such extensive recombination could occur for an extended period without rapidly consuming essentially all available reactant. It is not our experience that a recombiner can function partially and stably. The experimentally determined catalytic function for deuterium/oxygen recombination at 40°C of a catalyst sphere recovered from the explosion, was indistinguishable from that of unused catalyst; its catalytic function apparently was not impaired.

These facts can largely be accommodated by supplementing the hypothesis described above with the condition that the pressure in the cell at 844 hr, when

it was apparently open to the ambient, would have to have been in the range 10-30 atm.

The preexistence of an elevated pressure provides an inventory of gas to source the leak and still provide approximately 30 atm at 865 hr; substantially decreases the sensitivity of cell voltage as a monitor of cell pressure since such changes are determined mostly by $\ln(P/P^{o})$; and accommodates a more obvious recombiner function, since recombination can be assumed to occur by two competing mechanisms.

The issue of how and when the elevated pressure came into existence and why it was not observed, remains to be addressed. One plausible explanation is that the PTFE disk at the top of the cell was forced up against the top plate through which the electrical and pressure feedthroughs passed, acting as a seal that became increasingly effective as the internal pressure rose. Initial closure may have been accomplished after a rupture occurred in the pipe, thus providing a pressure gradient that would force the PTFE disk against the cell top.

Safety In Future Experimentation

As a result of our experience we currently base our experiment design philosophy on the following concepts:

(i) Passive metal recombiners should not be relied on to perform in any regular fashion, and must be presumed to operate at any time fully and stably, partially or intermittently.

(ii) All electrolysis cells should be placed in an explosion shielded environment that can withstand the effects of a hydrogen/oxygen explosion which results in a final pressure of at least ten times the maximum sustainable hydrostatic pressure of the cell; this includes protection from the blast and any fragmentation projectiles.

(iii) No cell shall be removed from the shielded environment until the cell has been shown to be at an internal pressure of 1 atm of an inert gas; in this respect, relying on a pressure gauge alone, is insufficient.

A cell design that meets the requirement in (ii) is shown in Figure 6.

REFERENCES

1. SRI Scientific Investigative Committee, 1992, The January 2, 1992, Explosion in a Deuterium/Palladium Electroytic System at SRI International.
2. Colton, J. and Jones, R., 1992, Metallurgical/Mechanical Aspects of Accident Investigation.
3. Crouch-Baker, S., McCarty, J., McKubre, M., Smedley, S., Tanzella, F., 1992, Chemical, Thermodynamic and Electrochemical Aspects of Accident Investigation.